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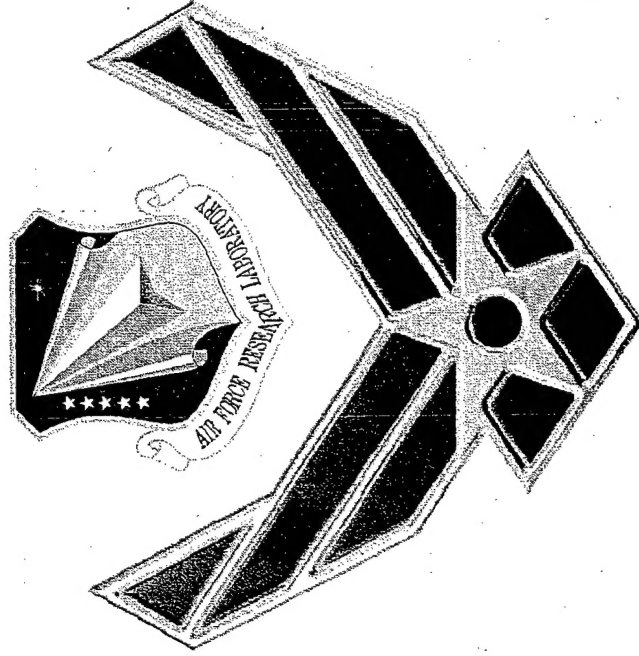
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# Computational Studies of Ionic Liquids

AFOSR Ionic Liquids Workshop

March 7-8, 2004



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# ***Collaborators***



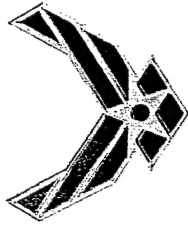
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# ***Outline***

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- 1. Introduction**
- 2. Structures and relative energies of  
1,5-diamino-1,2,3,4-tetrazolium cation**
- 3. Summary and Conclusions**



# Propellants Program General Approach

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics

## Experiments

Exploratory experiments

Identify target compounds

Calculate stability and performance

## Theory & modeling

Develop new synthesis methods

Attempt synthesis on small scale

Calculate possible synthesis routes

Measure properties & compare with predictions

Characterize new materials

Model spectral fingerprints

Optimize synthesis, devise test methods

Scale up and test

Transition to Industry

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# ***Modeling & Simulation of New Chemical Propellants***

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \right] \Psi_{el} = E_{el} \Psi_{el}$$

**Is a proposed propellant molecule/material stable?**

Structure optimization, verification as local minimum

**What is its energy content?**

Heats of formation and combustion

**How may it be synthesized? How will it react/decompose/combust?**

Reaction pathways

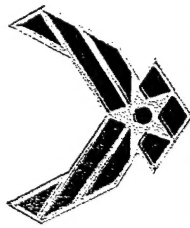
**How will we know if we've synthesized it?**

Vibrational spectra (IR, Raman, isotopic shifts)

NMR chemical shifts

Electronic spectra

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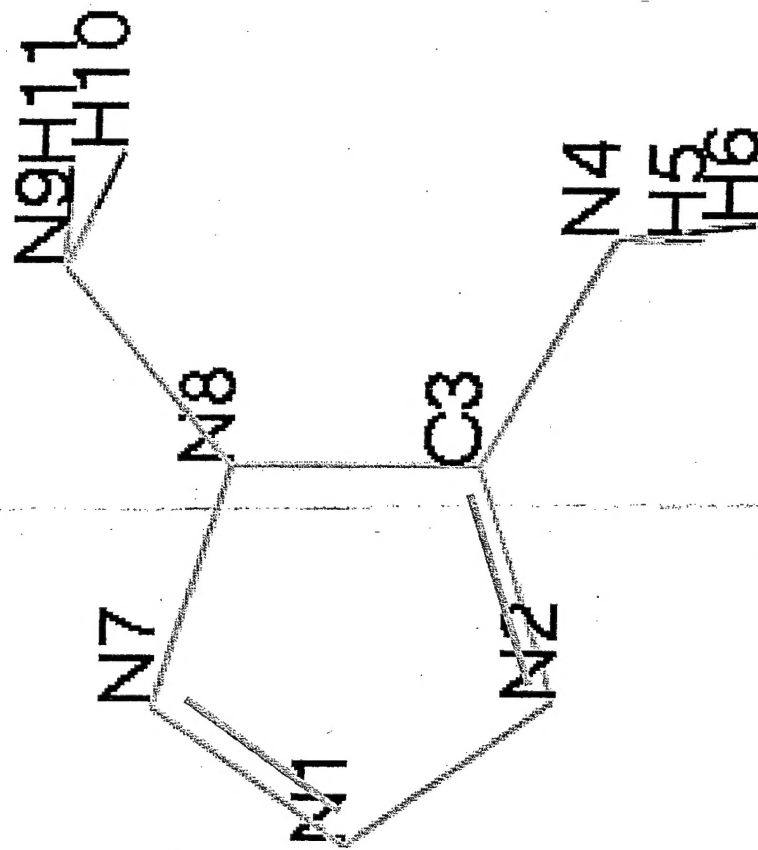


# 1,5-diamino-1,2,3,4-tetrazole

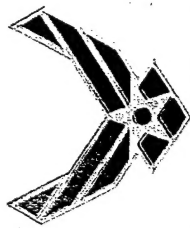


What is the preferred N-protonation site?

What level of theory is required?



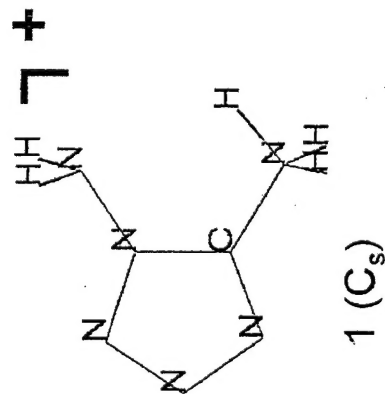
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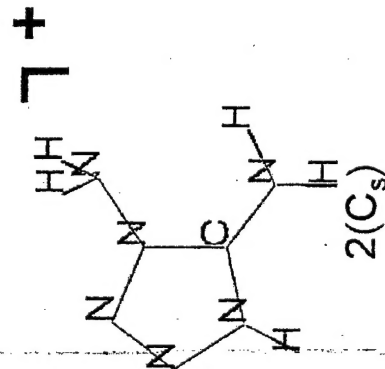
# B3LYP(3) Structures and Relative Energies (kcal/mol)



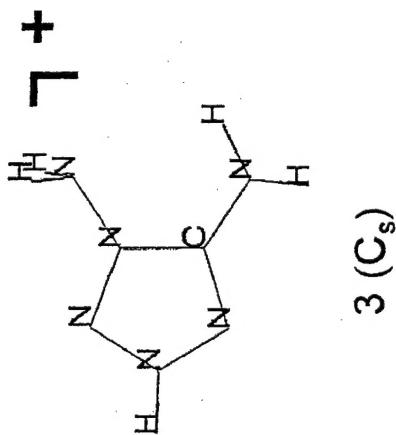
B3LYP(3)/6-311G(d,p) [B3LYP(3)//aug-cc-pvtz//B3LYP]



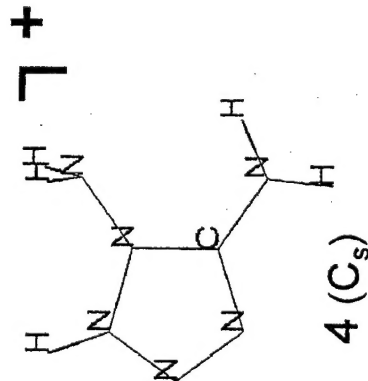
35.5 [36.6]



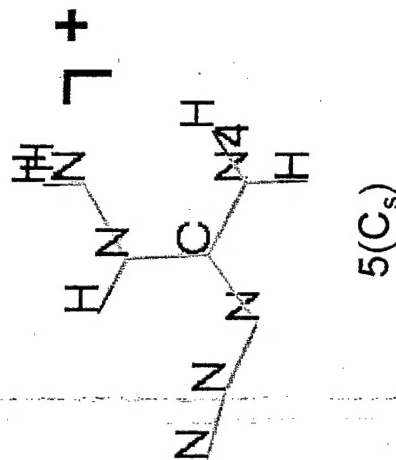
2.1 [3.2]



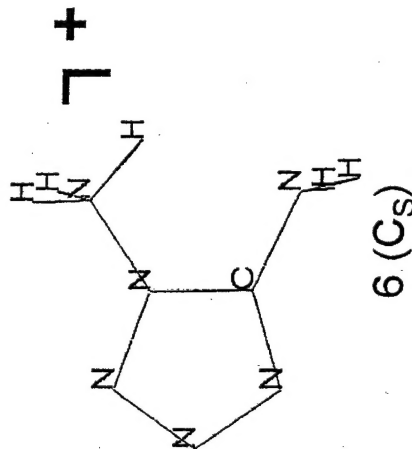
5.0 [5.6]



18.0 [18.6]



0.0 [0.0]



42.9 [43.9]

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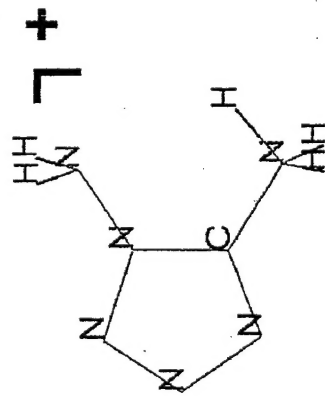




# MP2 Structures and Relative Energies (kcal/mol)

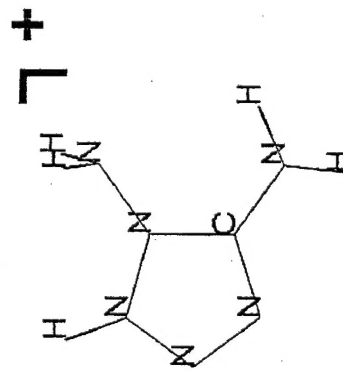


## MP2/6-311G(d,p) [CCSD(T)/6-311G(2df,p)//MP2]



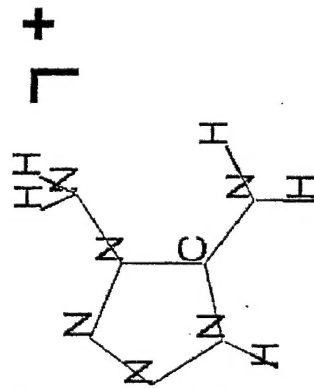
1 ( $C_s$ )

26.9 [29.6]



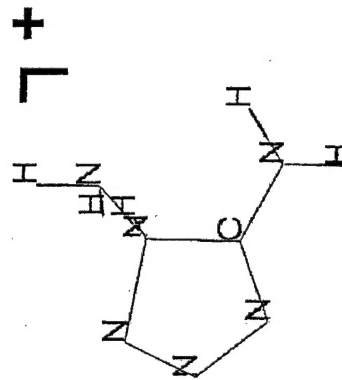
4 ( $C_1$ )

18.7 [16.8]



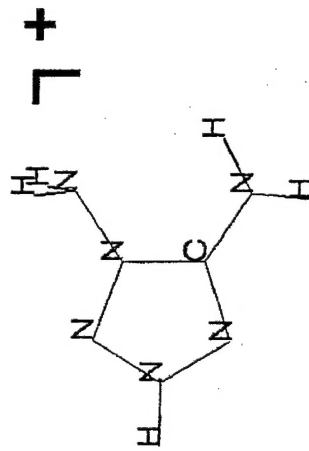
2 ( $C_1$ )

0.6 [0.0]



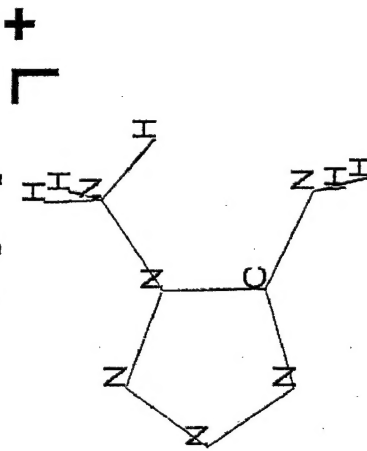
2 ( $C_1$ )

51.2 [45.6]



3 ( $C_1$ )

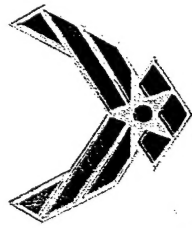
0.0 [3.3]



3 ( $C_s$ )

36.4 [38.0]

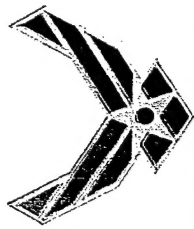
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# Summary of Relative Energies (kcal/mol)

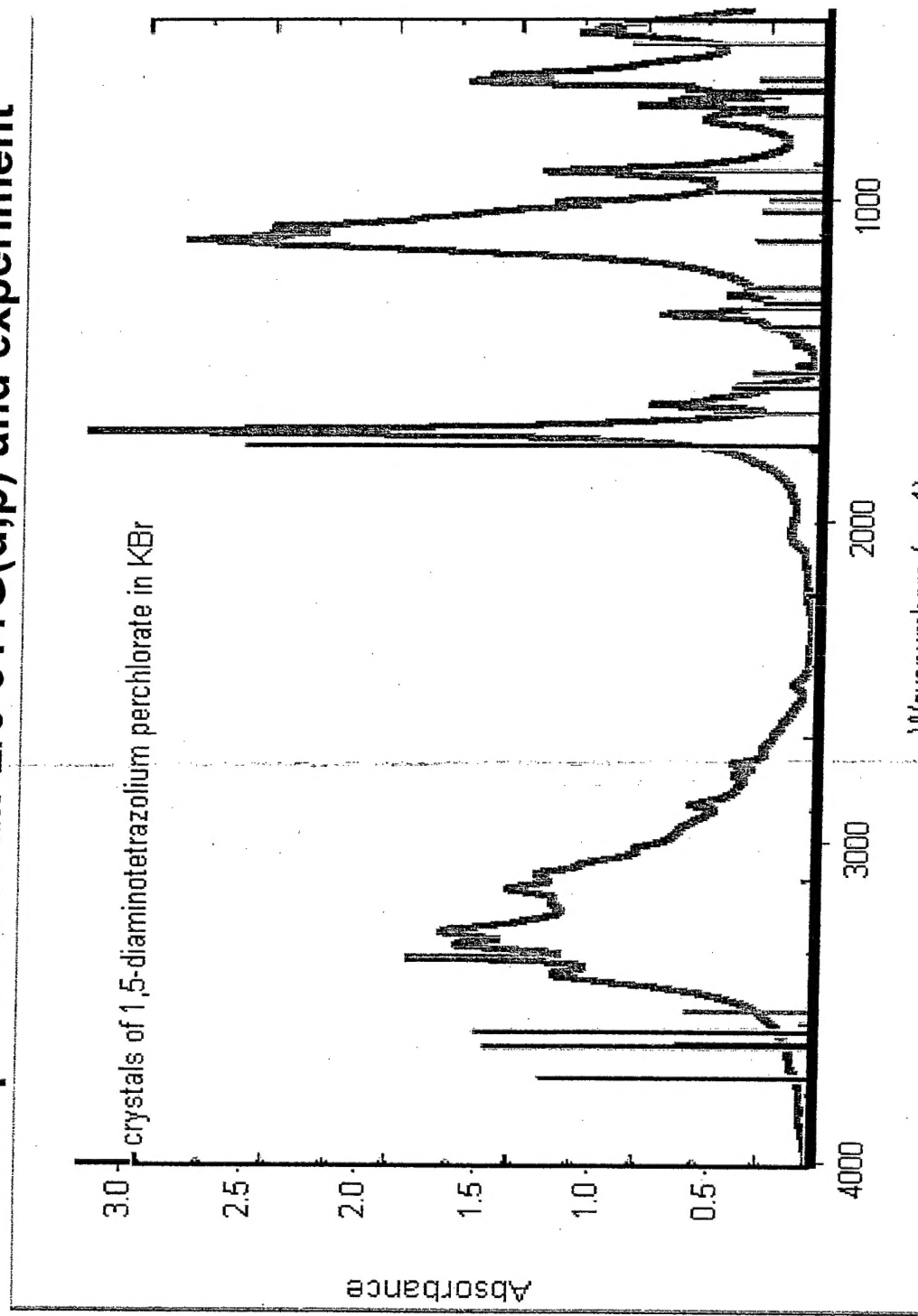


	1	2	3	4	5	6
B3LYP(3)/6-311G(d,p)	35.5	2.1	5.0	18.0	0.0	42.9
B3LYP(3)/6-311G(2df,p)//	-----	-----	-----	TBD	-----	-----
B3LYP(3)/aug-cc-pvtz//	36.6	3.2	5.6	18.6	0.0	43.9
MP2/6-311G(d,p)	26.9	0.6	0.0	18.7	51.2	36.4
MP2/6-311G(2df,p)//	-----	-----	-----	TBD	-----	-----
MP2/aug-cc-pvtz//	-----	-----	-----	TBD	-----	-----
CCSD(T)/6-311G(2df,p)//MP2	29.6	0.0	3.3	16.8	45.6	38.0

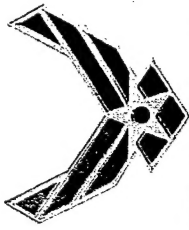


# Infrared Vibrational Spectra

## Comparison of MP2/6-311G(d,p) and experiment



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## Summary & Conclusions



- The structures and relative energies of the six possible N-protonated structures of the 1,5-diamino-1,2,3,4-tetrazolium cation have been computed at the B3LYP(3)/6-311G(d,p) and MP2/6-311G(d,p) levels of theory. Relative energies have been refined at the B3LYP(3), MP2, and CCSD(T) levels, using the 6-311G(2df,p) and aug-cc-pvtz basis sets.
- Isomers 2 (4H) and 3 (3H) are essentially degenerate at all levels of theory.
- B3LYP predicts isomer 5 (1H) to ring open to form an azide ( $\text{NH}_2\text{NHC}(\text{N}_3)=\text{NH}_2$ ).
- CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) calculations predict structure 2 to be the most stable isomer, in agreement with the X-ray crystal structure of the perchlorate salt.

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